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**WO 01/96494 A1**

(54) Title: **CHIRAL ADDITIVES FOR CHOLESTERIC DISPLAYS**

(57) Abstract: A unique class of chiral additive materials is disclosed for use in cholesteric displays that possess a helical twist power substantially independent of temperature. The additives have a solubility and a helical twist power large enough to be used as a single chiral component with little dilution of the physical properties of the nematic liquid crystal host mixture. The chiral additives may be used in combination with non-chiral additives to provide a helical twisting power substantially independent of temperature suitable for cholesteric displays.

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## CHIRAL ADDITIVES FOR CHOLESTERIC DISPLAYS

### STATEMENT OF GOVERNMENT INTEREST

The invention described herein was made in the performance of work under Contract  
5 No. DMI9903655 awarded by the National Science Foundation. Thus, the Government of the  
United States has certain rights in this invention.

### BACKGROUND OF THE INVENTION

#### Field of the Invention

10 The present invention relates to a unique class of chiral compounds for liquid crystals,  
and to liquid-crystalline mixtures containing such chiral compounds, and to their use for  
cholesteric displays and the resulting devices.

#### Description of the Related Art

15 Cholesteric flat-panel displays are currently under development because of their low  
power consumption, bright viewing characteristics at wide angles, and high-resolution  
capability at low cost. Their low-power consumption is a result of the bistable memory  
characteristic inherent in the technology. As described in the first U. S. Patents on this  
technology (See U.S. Patent Nos. 5,251,048, 5,384,067, 5,437,811, and 5,453,863), each  
20 pixel of the display can exist in a stable color reflective state with any desired reflective  
intensity or brightness (gray-scale) without any applied power. The degree of brightness is  
electronically selected by a pulse. A unique feature described in those inventions, is the  
existence of a threshold in the electronic response to a pulse such that a matrix of pixels can  
be multiplexed to achieve a high resolution display at low cost without the need of transistor  
25 elements (active matrix) at each pixel. Because of the low power and reflective brightness  
characteristics, cholesteric displays are used in portable or handheld applications where long  
battery life and versatile viewing capabilities are important.

The reflective properties of cholesteric liquid crystals have been generally known for  
30 many years. Sometimes called a chiral nematic, a cholesteric liquid crystal achieves its color  
reflective property because the molecules are arranged in a helical twist pattern with a

periodicity (pitch length) equal to the wavelength of light in the material. The first materials explored with this property were the cholesterol esters. These materials are not only chiral but also liquid crystalline and reflect iridescent colors when the periodicity of the twist corresponds to a reflective wavelength from 400nm to about 700nm ["Cholesteric Structure –  
5 II: Chemical Significance", p105 – 119, J. L. Fergason, N. N. Goldberg, R. J. Nadalin, *Liquid Crystals*, Ed. G. H. Brown, G. J. Dienes, M. M. Labes, Gordon and Breach Science Publishers, New York (1966)]. The materials were therefore called cholesteric liquid crystals, a name still used today even though cholesterol materials are seldom used today. Instead, a mixture of chiral and achiral compounds is used as discussed by Gottarelli *et al.* ["Induced  
10 Cholesteric Mesophases: Origin and Application, G. Gottarelli, G. P. Spada, *Mol. Cryst. Liq. Cryst.*, 123, 377 – 388 (1985)]. Achiral liquid crystalline compounds make up a nematic liquid crystalline host mixture, which has no helical twist by itself. To this host nematic is added a chiral compound to twist up the nematic material into one of a cholesteric structure, hence the name chiral nematic.

15  
The helical arrangement of the molecules provides a self-assembled stack of dielectric layers because of the anisotropy of the refractive index of the molecules. The index of refraction continuously varies along the stack by as much as 0.25 depending upon the nematic material. Because of the helical nature of the refractive index in the layer, the stack  
20 will reflect one circular component of a selected bandwidth of colored light. A right handed twisted planar texture will therefore decompose incident unpolarized white light into its right and left components by reflecting the right hand component and transmitting the left. A left-handed twisted material will do the opposite. A left-hand display cell stacked on top of a right-hand cell, both with the same pitch length, will reflect all of the incident light.

25  
According to Bragg's law, the wavelength  $\lambda$ , of the selective reflection is given by the equation:  $\lambda = np$  where  $p$  is the pitch of the helical structure and  $n$  is the average refractive index of the liquid crystal mixture. In mixtures of a nematic liquid crystal with the chiral additive, the reciprocal of the pitch length is approximately proportional to the concentration  
30  $X$ , of the chiral compound,  $p^{-1} = \beta X$  with  $\beta$  being the helical twisting power (HTP).

Conventional chiral additives available today have twisting powers typically of  $\beta < 15\mu\text{m}^{-1}$  when  $X$  is measured in weight percent.

Certain dimethanoldioxolane derivatives have been described in the literature as  
5 possessing large HTP values. E.g., "TADDOLs with Unprecedented Helical Twisting Power  
in Liquid Crystals", H. G. Kuball, B. Weiss, A. K. Beck, D. Seebach, *Helvetica Chimica  
Acta*, 80, 2507-2514 (1997); "TADDOLs Under Closer Scrutiny - Why Bulky Substituents  
Make it All Different", A. K. Beck, M. Dobbler, D. A. Plattner, *Helvetica Chimica Acta*, 80,  
2073-2083 (1997); and in US Patent 5,637,255. Like other chiral additives, they are also  
10 known to generally possess large temperature dependent values of  $dp/dT$  and, hence,  $d\lambda/dT$ .  
Their temperature dependencies tend to be positive in that the pitch length increases with  
increasing temperature, causing a cholesteric material to change from blue to red reflecting.  
Furthermore, the temperature dependence  $dp/dT$  has been shown to depend on the material of  
the host nematic. See "TADDOLs with Unprecedented Helical Twisting Power in Liquid  
15 Crystals", H. G. Kuball, B. Weiss, A. K. Beck, D. Seebach, *Helvetica Chimica Acta*, 80,  
2507-2514 (1997).

In order for flat-panel displays to be useful for portable applications, it is necessary  
for the display be operable over a wide range of temperatures. Outdoor temperatures can  
20 range from  $-20^{\circ}\text{C}$  to  $+50^{\circ}\text{C}$  depending on the environment. It would be advantageous if the  
reflected colors did not change over this temperature range. Implementing this desirable  
characteristic is not a straightforward task, since nearly all cholesteric liquid crystalline  
materials are well known to exhibit reflective colors that vary strongly with changes in  
temperature. Depending on the shape or chemical structure of the chiral molecule, the pitch  
25 length  $p$  and, hence, the peak reflective wavelength  $\lambda$ , can increase with temperature  
( $+d\lambda/dT$ ) or decrease with temperature ( $-d\lambda/dT$ ). Also, in many cases,  $d\lambda/dT$  is not linear over  
the temperature range of the cholesteric phase.

It should be mentioned at this point that the measurement for the temperature  
30 dependence of the pitch is performed using test cells, each of which is  $5\mu\text{m}$  thick, and has a  
hard coat layer on both substrates. There is also an unrubbed polyimide surface on top of the

hard coat layers. The measurement for the temperature dependence of the pitch is performed in the following manner. A collimated light is incident on the display at surface normal and the reflected light is detected at 45°. The display is scanned in the wavelength band that includes the peak-reflected wavelength, e.g., 400nm to 700nm, or 700nm to 1500nm. The cell is switched to the planar texture at each test temperature. The measurement is performed from -20°C to +70°C in 10°C intervals. It should be noted that, for the purposes of a flat temperature dependence, only a portion of the test temperature range, i.e., temperatures between +10°C to +50°C, are considered. In any event, the maximum change in peak reflected wavelength is then recorded. A mixture is considered to exhibit temperature independent color behavior if the maximum change in the peak reflection wavelength is 30nm or less across the temperature range of +10°C to +50°C.

It has been shown that cholesteric displays fabricated using a mixture of two or more chiral compounds as additives can be made to produce a helical twist power and, hence, reflective wavelength that is independent of temperature by combining a chiral compound that has a  $+d\lambda/dT$  with one with a  $-d\lambda/dT$ . U.S. Patent No. 5,309,265 describes a means of achieving a temperature independent  $\lambda$  by combining a plurality of chiral compounds, where both compounds exhibit the same twist sense.

It will be noted that there are a number of factors that preclude employing many previously known chiral compounds in liquid crystals. First of all, a chiral compound must be soluble in the nematic liquid crystal host material; many compounds are simply not soluble or only weakly soluble and, thus, cannot be used. In compounds that are soluble, they may adversely affect the nematic material by substantially reducing the temperature range of the liquid crystalline phase. If the chiral compound has an HTP that is too low, it may be necessary to add a large quantity of the additive which can dilute some of the desirable physical properties of the host nematic needed for the cholesteric display.

Consequently, a need still exists for a chiral additive, which is readily soluble in a nematic host mixture and which can be used individually (i.e., without needing to be combined with other chiral materials) for cholesteric displays that provides a high helical

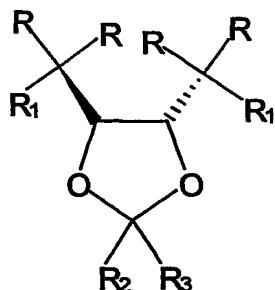
twisting power, substantially independent of temperature in operating ranges suitable for the cholesteric displays. What is also needed is a cholesteric display exhibiting a high helical twisting power, which is substantially independent of temperature in operating ranges suitable for the cholesteric displays, which display includes at least one chiral additive, which is readily soluble in a nematic host mixture. In some cases it would be desirable if the temperature dependence of the cholesteric display could be tailored by the addition of a second additive, e.g., either an achiral compound or a second chiral additive different from the first chiral additive, where the twist senses of the first and second chiral additives are opposite to one another.

### SUMMARY OF THE INVENTION

The above and other objectives are fulfilled by the present invention which concerns a unique class of chiral compounds that can be used alone as the optically-active additive or dopant in nematic liquid crystals to achieve a reflective wavelength that is temperature independent or essentially temperature independent, i.e., a  $d\lambda/dT$  approaching zero in value, yet without significantly reducing the temperature range of the liquid crystalline phase, or diluting or otherwise adversely affecting its needed physical properties for liquid crystal implementations.

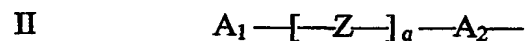
The inventive compounds are derivatives of dioxolanes and have the molecular structure generally indicated in Fig. 1 and reproduced below as general formula I.

I.



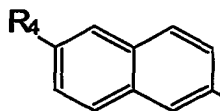
The R, R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> substitutions on the molecule of general formula I control the temperature dependence of the twisting power in the nematic host mixture in a surprisingly superior fashion. Generally, the R<sub>2</sub> and R<sub>3</sub> groups at the number 2 position of the dioxolane

ring independently are hydrogen, methyl or another lower alkyl group, or a substituted aryl or biaryl unit, while the  $R_1$  groups independently each are a hydroxyl, alkoxy, aryloxy, or arylalkoxy group. The R groups in general formula I indicate a group of general formula II, which is as follows:

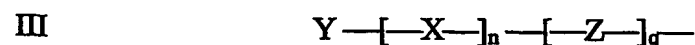


where  $A_1$  is an aromatic group, an acyclic aliphatic group, or an alicyclic group (e.g., a mono- or polycyclic aryl group, a straight chain or branched chain alkyl group, an arylalkyl group, an arylalkenyl group, a cycloalkyl group, a cycloalkenyl group), and  $A_1$  can be a substituted or unsubstituted group. For example,  $A_1$  can be benzyl, cinnamyl, phenethyl, cyclohexyl, and the like. Z is a group selected from -O-, -OCO-, or -S-, and the coefficient q is 0 or 1. Z can also be  $(CH_2)_nO$  with the coefficient n being 0 to 5 and the coefficient q being 1.  $A_2$  is a bivalent radical of naphthalene that may additionally be substituted. Preferably,  $A_2$  is a bivalent radical (2,6- or 1,5-disubstituted) of naphthalene, which may be unsubstituted or substituted (e.g., methyl, cyano, halogeno, amino, nitro, or hydroxyl substituents). The ring structure of  $A_2$ , or  $A_1$  if it is cyclic, optionally can be heterocyclic, such as by replacement of one or more CH member(s) of the ring structure with N, O and/or S (e.g., a bivalent radical of quinoline, xanthene, carbazole, or acridine).

In one preferred embodiment, each R substituent of general formula I is independently selected as:



where  $R_4$  can be represented by general formula III as follows:



where n is an integer value of 0 or 1 or more, X is  $-\text{CH}=\text{CH}-\text{CH}_2-$ , or  $-(\text{CH}_2)_m-$  where m is an integer value of 1, 2, 3, or more. Y is a radical of an aromatic hydrocarbon, an acyclic aliphatic hydrocarbon, or an alicyclic hydrocarbon group (e.g., a mono- or polycyclic aryl group, a straight chain or branched chain alkyl group, a cycloalkyl group, a cycloalkenyl group, and the like), and Y can be a substituted or unsubstituted group. Z and q have the same  
5 respective meanings as defined above relative to general formula II.

In one preferred embodiment,  $R_4$  is an aryloxy, an arylalkoxy, an arylalkyleneoxy, or an arylalkenyleneoxy group. Examples of  $R_4$  advantageously may include, for instance,  
10 benzyloxy ( $\text{C}_6\text{H}_5-\text{CH}_2-\text{O}-$ ), cinnamyloxy ( $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{CH}_2-\text{O}-$ ), phenethyloxy ( $\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}_2-\text{O}-$ ), and the like, where  $R_1$  is a hydroxy group and  $R_2$  and  $R_3$  are methyl groups.

Additionally, the specific structures of the four R groups present in formula I or Fig. 1 can be identical to each other or they can independently vary from each other within the  
15 guidelines indicated above and herein.

The inventive optically-active, chiral additives according to the formula of Fig. 1 contain a sufficiently high helical twisting power (HTP) so that only a relatively small amount of the chiral additive is required to twist the nematic phase to a pitch length where it  
20 reflects wavelengths in the visible or infrared portion of the electromagnetic spectrum. On the other hand, the HTP of the additive is not inordinately high either, so that the invention can avoid undesired gradients in concentration, which could cause undesired inhomogeneities in the display. The present invention thereby avoids the need to combine separate types of chiral compounds in order to achieve a very high degree of temperature independence. While the  
25 present invention does not necessarily exclude the possibility, and in fact does contemplate, use of mixtures of different inventive chiral compounds within the scope of the formula of Fig. 1, the important point is that the inventive chiral compounds can be effectively used singly in a liquid-crystalline nematic mixture deployed in a light modulating apparatus to avoid the need for chiral additive combinations.

30

### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is the general chemical structure of the dioxolane derivatives according to the present invention, where the  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  substituents control the temperature dependence of the twisting power in a superior manner.

5

Fig. 2 is the chemical structure of a preferred inventive compound embodied by the formula of Fig. 1, viz., (4R,5R)-2,2-dimethyl- $\alpha,\alpha,\alpha',\alpha'$ -tetrakis[6-(benzyloxy)naphth-2-yl]-1,3-dioxolane-4,5-dimethanol, which has been experimentally demonstrated to provide low  $d\lambda/dT$  in certain nematic host mixtures.

10

Fig. 3 is a graph showing the peak reflection wavelength (nm) versus temperature results for experimental tests performed with respect to a variation in color for two compounds in the E44 nematic host mixture. A substitution on the naphthalene units shows a dramatic change in the  $d\lambda/dT$  results.

15

Fig. 4 is a graph showing the peak reflection wavelength (nm) versus temperature results for experimental tests performed on the dimethanoldioxolane compound from Fig. 2 in E44 nematic host mixture tested with and without UCN additive.

20

### DETAILED DESCRIPTION OF THE INVENTION

In this invention, a new class of derivatives of dioxolanes embodied by the formula of Fig. 1 has been discovered that provide a substantially temperature independent  $dp/dT$  over a wide operating temperature range when added to nematic liquid crystalline mixtures with physical properties that are useful in cholesteric displays, including commercially viable cholesteric displays. The inventive chiral compounds are especially useful as additives to nematic liquid crystals for use in cholesteric displays to achieve needed properties for their practical use, particularly in portable device applications. Significantly, this invention provides this utility while only requiring the use of a single type of chiral additive compound within the scope of the invention, as described herein, and without requiring a mixture of different types of chiral additives.

30

Commercially viable displays require a liquid crystal mixture that has a dielectric anisotropy, birefringence and desired elastic and viscosity coefficients to provide a display with suitable brightness, contrast, and speed. The dielectric anisotropy and viscosity must be such that low voltage pulses can be used to reduce the cost of the electronic drive chips as well as implement drive schemes and waveforms for rapidly addressing the display. The birefringence has to be large to provide high brightness. Furthermore, the materials must not provide undesirable features to the display such as image sticking or phase separation. Cholesteric displays therefore require very special cholesteric materials. Cholesteric displays incorporating the inventive dioxolane derivatives satisfactorily meet all these criteria and requirements, while providing superior temperature independence performance and so forth.

Namely, the invention provides chiral compound additives to nematic liquid crystals that provide at least the following features important for cholesteric displays:

1. Solubility in nematic liquid crystals that have the physical properties necessary for cholesteric displays.
2. Possess a helical twist power (HTP) generally ranging from  $15 \mu\text{m}^{-1}$  to  $200 \mu\text{m}^{-1}$ , and more usually from  $30 \mu\text{m}^{-1}$  to  $90 \mu\text{m}^{-1}$ . HTP values in this range are not so small as to dilute the important physical properties of nematic liquid crystals when twisted to reflect light in the visible spectrum. In addition, these values are not so large that slight inhomogeneities in the mixture caused by phase separation can disfigure the display.
3. Provide a substantially temperature independent HTP in the cholesteric phase over the operating temperature range of cholesteric displays of commercial value.
4. Do not decompose under ultraviolet light of exposures under common environmental conditions.
5. Do not chemically react with the host nematic liquid crystal.
6. Possess the property that the temperature dependence can be modified by the addition of an achiral additive to the nematic liquid crystal. Such an additive may or may not possess a liquid crystalline phase.

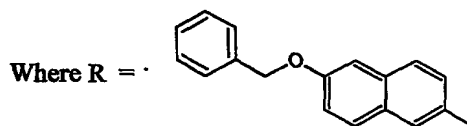
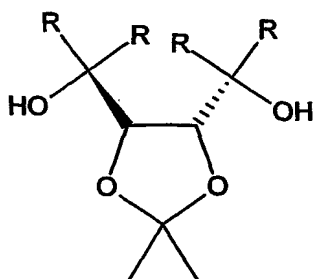
As compared to the competing contemporarily available chiral additives that have twisting powers typically of  $\beta < 15\mu\text{m}^{-1}$  when  $X$  is measured in weight percent, the new soluble chiral additive materials, invented here, have values of  $\beta$  approaching  $80\mu\text{m}^{-1}$ . This is a substantial improvement since the concentration of the chiral additive in this invention can be so small as to have a near negligible effect on the physical properties of the nematic liquid crystal.

Chiral nematic liquid crystalline materials within the scope of this invention, which include an inventive chiral additive and a nematic host mixture, can be implemented in cholesteric liquid crystal displays, electro-optical cells, and light modulating apparatuses in manners, arrangements and/or systems consistent with the descriptions, such as set forth in U.S. Patent Nos. 5,251,048, 5,384,067, 5,437,811, and 5,453,863, whose descriptions are incorporated by reference.

## EXAMPLES

### Synthesis Scheme for Chiral Additive:

One illustrative inventive compound, (4R,5R)-2,2-dimethyl- $\alpha,\alpha,\alpha',\alpha'$ -tetrakis[6-(benzyloxy)naphth-2-yl]-1,3-dioxolane-4,5-dimethanol, is shown in Fig. 2 and is reproduced below. The dimethanoldioxolane has 2,6-substituted naphthalene units.



The inventive compound of Fig. 2 was synthesized according to the following protocol with reference to the reaction Scheme I provided below.

### Synthesis of 2-(Benzyloxy)-6-bromonaphthalene (2) intermediate:

A mechanically stirred mixture of 6-bromonaphth-2-ol (10.00g, 0.04483mol), benzyl bromide (6.97g, 0.0408mol), potassium carbonate (11.26g, 0.08147mol) and butan-2-one

(350ml) was heated under reflux for 24 hrs. (GLC and TLC analyses revealed a complete reaction). The potassium carbonate was filtered off and the filtrate was washed with water before being dried (MgSO<sub>4</sub>). The drying agent was filtered off and the solvent was removed *in vacuo* to give a pale orange solid. The crude product was crystallized twice from ethanol and was dried *in vacuo* (P<sub>2</sub>O<sub>5</sub>, CaCl<sub>2</sub>, paraffin wax, 48h) to afford white crystals.  
Yield = 11.97g (94%), mp 113-114°C.

**Synthesis of product compound - compound (4):**

**(4R,5R)-2,2-dimethyl- $\alpha,\alpha,\alpha',\alpha'$ -tetrakis[6-(benzyloxy)naphth-2-yl]-1,3-dioxolan-4,5-dimethanol (4):**

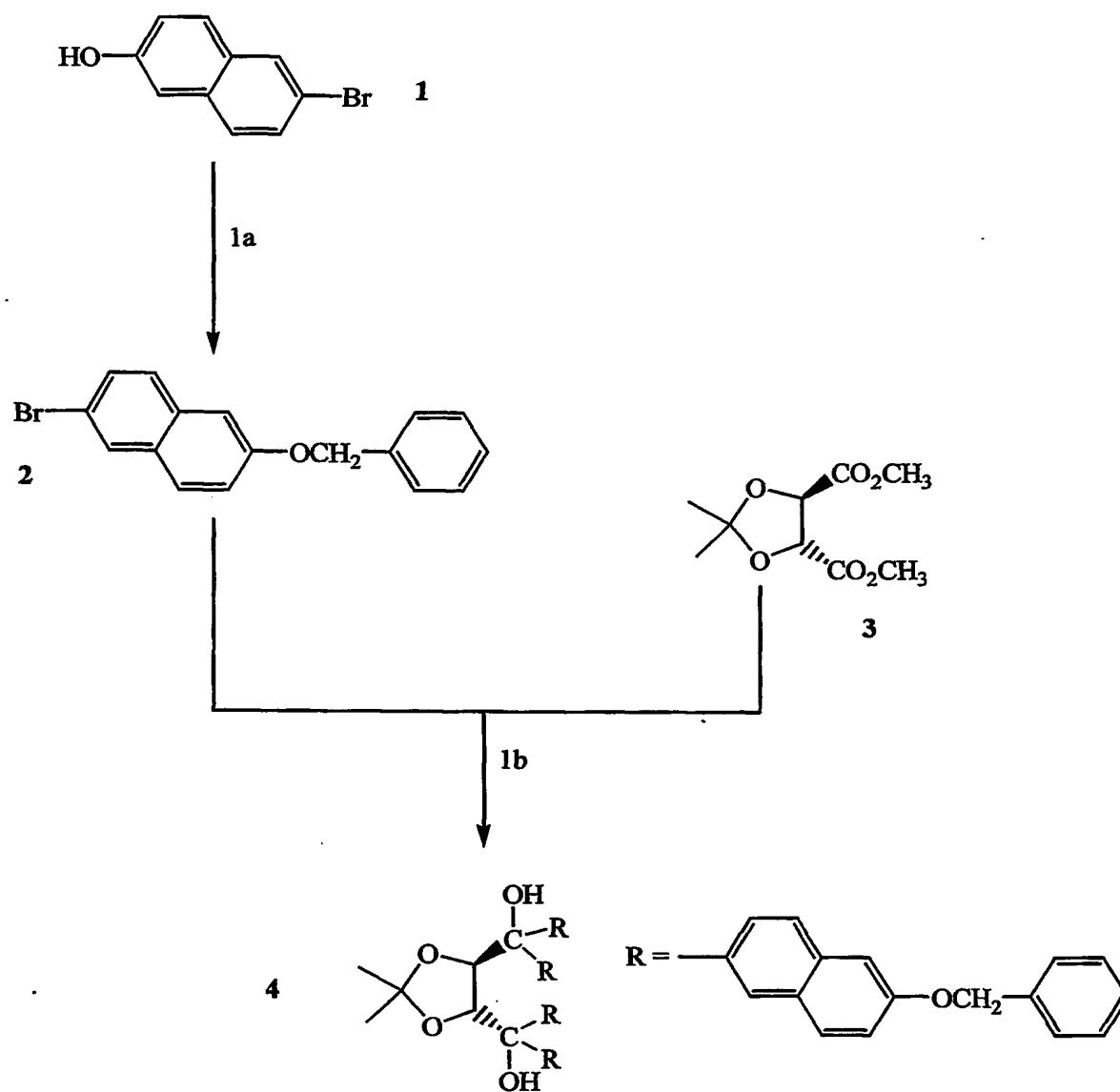
n-Butyllithium (5.37ml, 2.5M in hexane, 0.0134mol) was added dropwise at -74°C to -77°C to a mechanically stirred, cooled (-77°C) solution of compound 2 (4.20g, 0.0134mol) in dry tetrahydrofuran (350ml) under dry argon. Once the addition was complete, the reaction mixture was maintained under these conditions for a further 2 hrs. (GLC analysis revealed a complete reaction) before the reaction mixture was allowed to warm to -25°C.

2,3-O-Isopropylidene-L-tartrate (0.73g, 0.03345mol) was added to the reaction mixture at -20°C to -25°C (exothermic) and the reaction mixture was allowed to warm to room temperature. The reaction mixture was stirred at room temperature for a further 15 hrs. before saturated ammonium chloride (60ml) was added and the mixture stirred for a further 4 hrs. The reaction mixture was washed with diethyl ether (3 x 75ml) and the combined organic washings were dried (MgSO<sub>4</sub>). The drying agent was filtered off and the solvent was removed *in vacuo* to give an orange semi-solid.

The crude product was purified twice by column chromatography [silica gel / hexane, ethyl acetate, 4:1] followed by further chromatography [silica gel / hexane, diethyl ether, 4:1]. The product was crystallized from toluene to afford a pale yellow solid, which was dried *in vacuo* (P<sub>2</sub>O<sub>5</sub>, CaCl<sub>2</sub>, paraffin wax, 48h).

Yield = 7.30g (50%).

## Scheme 1



1a...Benzyl bromide,  $K_2CO_3$ .  
1b...(i) n-Butyllithium; (ii)  $NH_4Cl$ .

**Example 1:**

Experimental studies were performed on the dimethanoldioxolane compound (4) described above and of the structure shown in Fig. 2, and separately on (4R,5R)-2,2-dimethyl- $\alpha,\alpha,\alpha',\alpha'$ -tetrakis[naphth-2-yl]-1,3-dioxolane-4,5-dimethanol as a comparative compound, each in a E44 nematic host mixture, the results of which were plotted in Fig. 3 as a graph showing the peak reflection wavelength (nm) versus temperature. The respective cholesteric liquid crystal mixtures prepared for conducting these experimental studies were as follows.

**COMPOSITION 1 formulation:**

<u>Component</u>	<u>Component amt. (wt%)</u>
2-naphthyl as the R groups on the dimethanoldioxolane (comparative compound)	3.4%
E44	96.6%

**COMPOSITION 2 formulation:**

<u>Component</u>	<u>Component amt. (wt%)</u>
6-benzyloxynaphth-2-yl as the R groups on the dimethanoldioxolane (compound (4), Fig. 2 compound)	10.0%
E44	90.0%

It will be noted that E44 is commercially available nematic liquid crystal mixture that was obtained from Merck KgaA in Darmstadt, Germany through EM Industries in Hawthorne, New York. It will also be noted that the percentage of compound (4), and thus the percentage of E44, advantageously can be varied to achieve the desired reflective wavelength. For example, varying the percentage of compound (4) from 10 wt% to 2 wt% changes the reflective wavelength from the visible into the infrared. Finally, it will be noted that other additive materials can be included in the cell material to improve other cell properties.

As to the cholesteric display test cell arrangement used, both mixtures, i.e., Compositions 1 and 2, were vacuum filled in separate surface stabilized cholesteric displays with a 5 $\mu$ m cell spacing. To accomplish this, two glass plate substrates were put together using an epoxy material around the perimeters with the substrates separated by 5 micron spacers and a small hole left in the perimeter seal for introducing the liquid crystal. The inner  
5 faces of the glass substrates were coated with indium-tin oxide (ITO), a standard insulating layer, and a polyimide layer for liquid crystal alignment. The back plate was painted black. The liquid crystal mixture was vacuum filled into the provided cell so that each liquid crystal mixture was sandwiched between the two glass plate substrates.

The arrangement used to control the temperature of the liquid crystal mixtures samples being tested was as follows. A liquid nitrogen cryostat was used to control temperature on the test cells. The cryostat had a cold finger and a heater. The cryostat system was obtained from Janis Cryogenics. A white light source was used with a monochromator,  
15 both obtained from Oriel. A silicon detector was used to detect the light intensity. To measure the color, the cell was switched to the reflecting planar state at each temperature and the peak reflection wavelength was determined. The peak reflection wavelength of the cells was measured with incident light at the surface normal and reflected light detected at 45°. The switching pulse used had a magnitude (amplitude and width) high enough to transform the  
20 texture to the reflecting planar texture at each temperature. The pulse was an AC square pulse. Data points were typically acquired every 10°C from -20°C to about +70°C. The results of these measurements are plotted in Fig. 3.

The compound of Fig. 2 was found through these experimental studies to possess a  
25 substantially temperature independent HTP in the nematic mixture E44, which is suitable for cholesteric displays. The HTP for this compound at room temperature in E44 is 31 $\mu$ m<sup>-1</sup>. The HTP for the base compound (unsubstituted naphthalene units) is 91 $\mu$ m<sup>-1</sup>. A plot of the temperature dependence of the compound according to the present invention, a compound containing (4R,5R)-2,2-dimethyl- $\alpha,\alpha',\alpha',\alpha'$ -tetrakis[6-(benzyloxy)naphth-2-yl]-1,3-dioxolan-  
30 4,5-dimethanol, versus that of the comparative reference compound, i.e., a similar compound containing a small amount by weight of (4R,5R)-2,2-dimethyl- $\alpha,\alpha',\alpha',\alpha'$ -tetrakis[naphth-2-yl]-

1,3-dioxolane-4,5-dimethanol, which is strongly temperature dependent, is shown in Fig. 3. It should be noted that both molecules exhibit a linear temperature dependence from -20°C to +70°C.

- 5 In addition to the use of a single chiral additive, independence of the helical twisting power with temperature advantageously can be obtained by mixing two dioxolane materials that are structurally different and that exhibit opposite twist senses.

**Example 2:**

10 **ADDITIONAL STUDIES INVOLVING ACHIRAL COMPOUND ADDITIVE:**

The change in color of a liquid crystal mixture containing a chiral compound (viz., compound 4, Fig. 2 compound) and a host mixture (viz. E44) along with a small amount of an achiral non-liquid crystalline compound (undecyl cyanide at 4% by weight) was investigated. The components were mixed according to the following proportions as

15 **Composition 3:**

**COMPOSITION 3 formulation:**

<u>Component</u>	<u>Component amt. (wt%)</u>
6-benzyloxynaphth-2-yl as the R groups on the	11.0%
20 dimethanoldioxolane (compound (4), Fig. 2 compound)	
E44	85.0%
UCN (undecyl cyanide, C <sub>11</sub> H <sub>23</sub> CN)	4.0%

- 25 The resulting liquid-crystalline mixture containing the achiral additive was filled into a cell and tested using the arrangement described in Example 1. The results of these additional experiments investigating the possible effect of certain achiral additives to the liquid crystalline nematic mixture are shown in Fig. 4, and the plot of the results obtained for Composition 2 in Example 1 as indicated in Fig. 3 was included for sake of comparison. The inventive chiral dimethanoldioxolane compound used for these studies was used to twist the
- 30 nematic phase to a blue reflecting pitch length. Referring to Fig. 4, a subtle difference between the two curves was clearly evident. Without the achiral additive, the  $d\lambda/dT$  is nearly

flat with a slightly negative value, whereas with the achiral additive, the  $d\lambda/dT$  is nearly flat with a slightly positive value. The helical twisting power for the dimethanoldioxolane compound is similar for the two nematic mixtures in Fig. 4 with the additive host mixture showing a slightly higher HTP.

5

It should be noted that UCN is representative of a class of achiral compounds of the general structure  $R^1CN$  where  $R^1 = \text{alkyl}$ .  $R^1 = C_{11}H_{23}$ - for UCN itself.

Thus, a further discovery of this invention is that fine-tuning can therefore be performed using certain achiral non-liquid crystalline compounds added to a cholesteric system with a nematic host mixture and a single chiral compound.

For practicing this further embodiment, the achiral additive, namely, aliphatic nitriles, can be commercially obtained from Aldrich Chemicals or prepared by conventionally known methods. Useful alkyl nitriles as the achiral additive include 5C-17C alkanenitriles, and more preferably 8C-14C straight chain or n-alkane nitriles. One preferred alkyl nitrile is undecanenitrile, using IUPAC nomenclature (alternatively, referred to as undecyl cyanide, in common nomenclature). These achiral additives have been found to be effective in amounts of approximately 2 to 6 wt% of the overall liquid-crystalline mixture.

20

Although E44 was exemplified above, virtually any nematic host mixture, including cyanobiphenyls known in the art, can be used in the practice of this invention. The inventive chiral compounds are readily soluble, as required, in many commercially available nematic host mixtures.

25

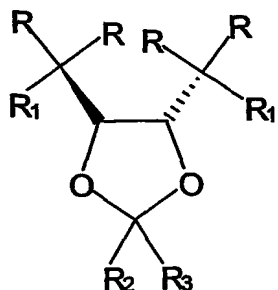
While this invention has been described in terms of its preferred embodiments, those skilled in the art will recognize that the invention can be practiced with modification within the spirit and scope of the appended claims.

## APPENDIX: References Cited

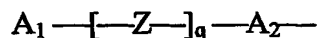
1. U.S. Patent No. 5,251,048: "Method and Apparatus of Electronic Switching of a Reflective Color Display", J. W. Doane, D.-K. Yang, October 1993.
2. U.S. Patent No. 5,384,067: "Grey Scale Liquid Crystal Material", J. W. Doane, D.-K. Yang, January 1995.
3. U.S. Patent No. 5,437,811: "Liquid Crystalline Light Modulating Device and Material", J. W. Doane, D.-K. Yang, L.-C. Chien, August 1995.
4. U.S. Patent No. 5,453,863: "Multistable Chiral Nematic Displays", J. West, D.-K. Yang, September 1995.
5. "Cholesteric Structure – II: Chemical Significance", p105 – 119, J. L. Fergason, N. N. Goldberg, R. J. Nadalin, *Liquid Crystals*, Ed. G. H. Brown, G. J. Dienes, M. M. Labes, Gordon and Breach Science Publishers, New York (1966)
6. "Induced Cholesteric Mesophases: Origin and Application, G. Gottarelli, G. P. Spada, *Mol. Cryst. Liq. Cryst.*, 123, 377 – 388 (1985)
7. U.S. Patent No. 5,309,265: "Short Pitch LC layer with a temperature Independent  $\lambda_0$  and Containing a Nematic LC Doped with Plural Chiral Additives Having the Same Twist Sense", R. Buchecker, J. Funfschilling, M. Schadt, May 1994.
8. "TADDOLs with Unprecedented Helical Twisting Power in Liquid Crystals", H.-G. Kuball, B. Weiss, A. K. Beck, D. Seebach, *Helvetica Chimica Acta*, 80, 2507-2514 (1997)
9. "TADDOLs Under Closer Scrutiny – Why Bulky Substituents Make it All Different", A. K. Beck, M. Dobbler, D. A. Plattner, *Helvetica Chimica Acta*, 80, 2073-2083 (1997)
10. U.S. Patent No. 5,637,255: "Chiral Dioxolanes", S. Kelly, M. Schadt, June 1997.

## WHAT IS CLAIMED IS:

1. An optically active compound of the formula:

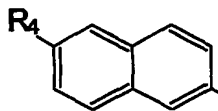


where the  $R_2$  and  $R_3$  groups are methyl, another lower alkyl group or an aryl or biaryl unit while the  $R_1$  groups independently each are a hydroxyl, alkoxy, aryloxy, or arylalkoxy group, the  $R$  groups each represent a group as follows:

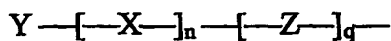


where  $A_1$  is an aromatic group, an acyclic aliphatic group, or an alicyclic group, and  $A_1$  can be a substituted or unsubstituted group,  $Z$  is a group selected from  $-O-$ ,  $-OCO-$ , or  $-S-$ , and the coefficient  $q$  is 0 or 1.  $Z$  may also be  $(CH_2)_nO$  where the coefficient  $n$  is 0 to 5 and the coefficient  $q$  is 1.  $A_2$  is a bivalent radical of a naphthalene group, and the cyclic structure of  $A_2$ , or  $A_1$  if it is cyclic, optionally can be heterocyclic, such as by replacement of one or more CH member(s) of the ring structure with N, O and/or S.

2. The optically active compound of claim 1, where each  $R$  substituent is independently selected as:



where  $R_4$  represents a group as follows:



where  $n$  is an integer value of 0 or 1 or more,  $X$  is  $-\text{CH}=\text{CH}-\text{CH}_2-$ , or  $-(\text{CH}_2)_m-$  where  $m$  is an integer value of 1, 2, 3, or more,  $Y$  is a radical of an aromatic hydrocarbon, an acyclic aliphatic hydrocarbon, or an alicyclic hydrocarbon, and  $Y$  can be a substituted or unsubstituted group, and  $Z$  and  $q$  have the same respective meanings as defined in claim 1.

5

3. The optically active compound of claim 2, where  $R_4$  is an aryloxy radical, an arylalkoxy radical, an arylalkyleneoxy, or an arylalkenyleneoxy radical.

10

4. (4R,5R)-2,2-dimethyl- $\alpha,\alpha,\alpha',\alpha'$ -tetrakis[6-(benzyloxy)naphth-2-yl]-1,3-dioxolane-4,5-dimethanol.

15

5. A liquid crystalline mixture, comprising:  
a liquid-crystalline base having liquid crystalline properties;  
at least one optically active compound of the formula as described in  
any of one of claims 1-4.

20

6. The liquid crystalline mixture according to claim 5, further including an achiral non-liquid crystalline compound.

7. The liquid crystalline mixture according to claim 6, wherein the achiral non-liquid crystalline compound comprises  $R^1-\text{C}\equiv\text{N}$ , where  $R^1$  represents an aliphatic group.

25

8. The liquid crystalline mixture according to claim 7, wherein  $R^1-\text{C}\equiv\text{N}$  comprises an alkylnitrile.

9. The liquid crystalline mixture according to claim 7, wherein  $R^1-\text{C}\equiv\text{N}$  comprises undecanenitrile.

30

10. An electro-optical cell comprising a layer including a liquid crystalline mixture as described in any one of claims 5-9 sandwiched between two substrate means, and means for applying an electric potential to the substrate means.

11. A light modulating apparatus comprising an electro-optical cell according to claim 10.

5 12. The light modulating apparatus according to claim 11, wherein the light modulating apparatus comprises a cholesteric display.

13. An electro-optical cell comprising:

a layer comprising:

10 at least 70 weight percent (wt%) nematic host mixture; and  
at least about 2 wt% (4R,5R)-2,2-dimethyl- $\alpha,\alpha',\alpha'$ -tetrakis[6-(benzyloxy)naphth-2-yl]-1,3-dioxolane-4,5-dimethanol;  
first and second substrates disposed above and below, respectively, the layer; and  
first and second conductors physically coupled to the first and second substrates,  
15 respectively, which permit an electrical potential to be applied across the layer.

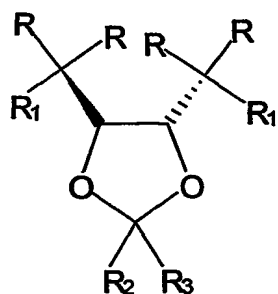
14. The electro-optical cell as recited in claim 13, wherein the layer further comprises about 2-6 wt% achiral material.

20 15. The electro-optical cell as recited in claim 13, wherein the layer further comprises a chiral material different from (4R,5R)-2,2-dimethyl- $\alpha,\alpha',\alpha'$ -tetrakis[6-(benzyloxy)naphth-2-yl]-1,3-dioxolane-4,5-dimethanol and having an opposite twist sense.

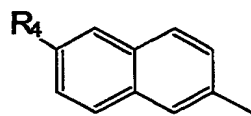
25 16. A light modulating apparatus comprising an electro-optical cell according to any one of claims 13-15.

17. The light modulating apparatus according to claim 16, wherein the light-modulating apparatus comprises a cholesteric display having a temperature independent reflective wavelength.

5 FIG. 1



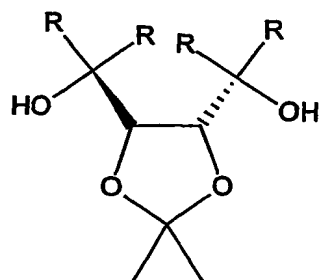
Where R =



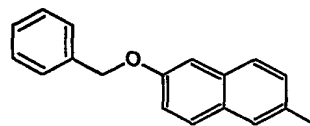
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FIG. 2

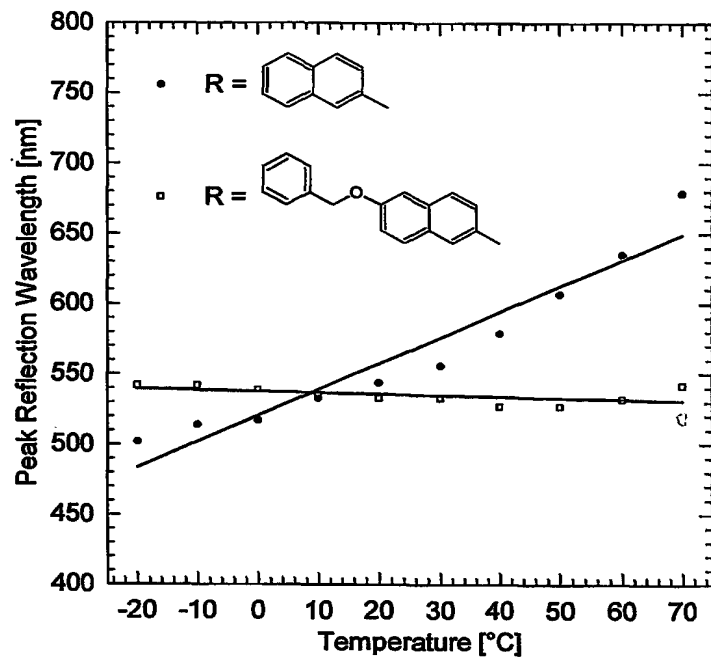


Where R =



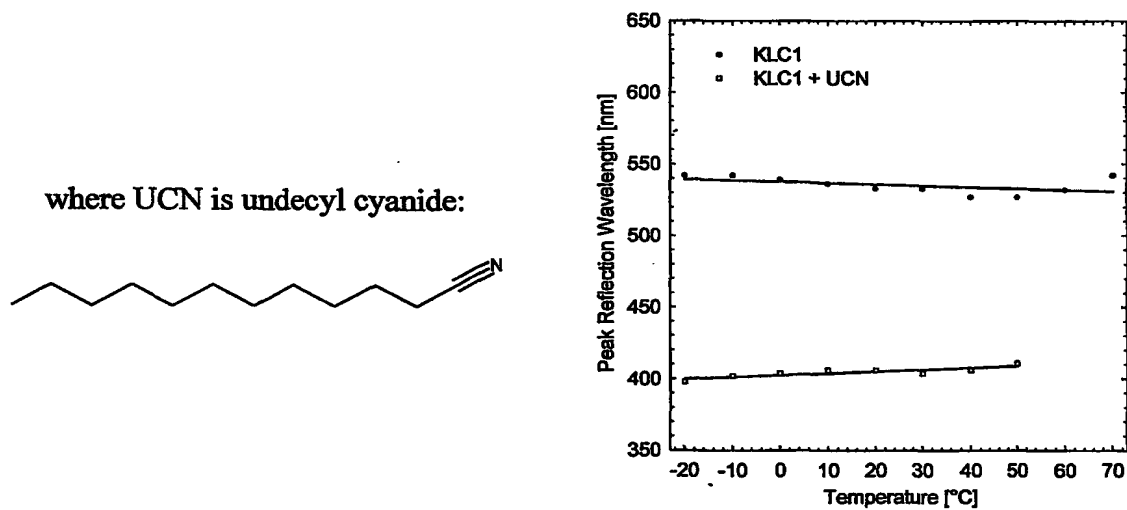
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FIG. 3



5

FIG 4



10

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US01/14842

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C09K 19/34, 19/32, 19/36; C07D 317/12

US CL : 252/299.01, 299.61, 299.62, 299.7; 428/1.1, 549/430, 453

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/299.01, 299.61, 299.62, 299.7; 428/1.1, 549/430, 453

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST 2.0, CAS online

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Kuball et al., "TADDOLs with Unprecedented Helical Twisting Power in Liquid Crystals", Helv. Chim. ACTA, Vol. 80, pages 2507-2514, 1997, see whole document	1, 5-6
Y		10-17
X	Chem. abstr., Vol. 124, No. 1996 (Columbus, OH, USA), page 9072, the abstract No. 9076r, Quinkert, Gerhard et al., " Total Synthesis with a Chirogenic Opening Move Demonstrated on Steroids with Estrane or 18-homoeestrane Skeleton". Helv. Chim. Acta 1995, 78(5), 1345-91 (Eng). see RN 170709-36-1.	1, 5



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	"I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"A" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

24 AUGUST 2001

Date of mailing of the international search report

11 OCT 2001

Name and mailing address of the ISA/US  
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Washington, D.C. 20231

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## REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

International Application No.

PCT/US 01/14842

International Filing Date  
08 JUN 2001PCT INTERNATIONAL  
APPLICATION RO/US

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference  
(if desired) (12 characters maximum)

KD-01-004PCT

Box No. I TITLE OF INVENTION  
CHIRAL ADDITIVES FOR CHOLESTERIC DISPLAYS

Box No. II APPLICANT ☐ This person is also inventor

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

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Teleprinter No.

Applicant's registration No. with the Office

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State (that is, country) of residence:  
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This person is applicant for the purposes of: ☐ all designated States ☒ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

DOANE, Joseph W.  
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This person is:

☐ applicant only

☒ applicant and inventor

☒ inventor only (If this check-box is marked, do not fill in below.)

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State (that is, country) of residence:  
United States of America

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

☒ Further applicants and/or (further) inventors are indicated on a continuation sheet.

Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:

☒ agent

☐ common representative

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

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Agent's registration No. with the Office  
34,231

☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

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If none of the following sub-boxes is used, this sheet should not to be included in the request.

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KHAN, Asad A.  
901 Admore Drive  
Kent, OH 44240, US

This person is:

- ☐ applicant only  
☒ applicant and inventor  
☒ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:  
Pakistan

State (that is, country) of residence:  
United States of America

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

SEED, Alexander J.  
4071 Baird Road  
Stow OH 44224-3601, US

This person is:

- ☐ applicant only  
☒ applicant and inventor  
☒ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:  
Great Britain

State (that is, country) of residence:  
United States of America

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only  
☐ applicant and inventor  
☐ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only  
☐ applicant and inventor  
☐ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.

Box No.V

DESIGNATION OF STATES

Mark the applicable check-boxes below; at least one must be marked.

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**Regional Patent**

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- ☐ **EA Eurasian Patent:** AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian
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- ☐ **OA OAPI Patent:** BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)

**National Patent (if other kind of protection or treatment desired, specify on dotted line):**

- |  |   |   |
|--|---|---|
| <input type="checkbox"/> AE United Arab Emirates               | <input type="checkbox"/> GE Georgia                                   | <input type="checkbox"/> MW Malawi                              |
| <input type="checkbox"/> AG Antigua and Barbuda                | <input type="checkbox"/> GH Ghana                                     | <input type="checkbox"/> MX Mexico                              |
| <input type="checkbox"/> AL Albania                            | <input type="checkbox"/> GM Gambia                                    | <input type="checkbox"/> MZ Mozambique                          |
| <input type="checkbox"/> AM Armenia                            | <input type="checkbox"/> HR Croatia                                   | <input type="checkbox"/> NO Norway                              |
| <input type="checkbox"/> AT Austria                            | <input type="checkbox"/> HU Hungary                                   | <input type="checkbox"/> NZ New Zealand                         |
| <input type="checkbox"/> AU Australia                          | <input type="checkbox"/> ID Indonesia                                 | <input type="checkbox"/> PL Poland                              |
| <input type="checkbox"/> AZ Azerbaijan                         | <input type="checkbox"/> IL Israel                                    | <input type="checkbox"/> PT Portugal                            |
| <input type="checkbox"/> BA Bosnia and Herzegovina             | <input type="checkbox"/> IN India                                     | <input type="checkbox"/> RO Romania                             |
|  | <input type="checkbox"/> IS Iceland                                   | <input type="checkbox"/> RU Russian Federation                  |
| <input type="checkbox"/> BB Barbados                           | <input checked="" type="checkbox"/> JP Japan                          |   |
| <input type="checkbox"/> BG Bulgaria                           | <input type="checkbox"/> KE Kenya                                     | <input type="checkbox"/> SD Sudan                               |
| <input type="checkbox"/> BR Brazil                             | <input type="checkbox"/> KG Kyrgyzstan                                | <input type="checkbox"/> SE Sweden                              |
| <input type="checkbox"/> BY Belarus                            | <input type="checkbox"/> KP Democratic People's Republic of Korea     | <input type="checkbox"/> SG Singapore                           |
| <input type="checkbox"/> BZ Belize                             | <input checked="" type="checkbox"/> KR Republic of Korea              | <input type="checkbox"/> SI Slovenia                            |
| <input type="checkbox"/> CA Canada                             | <input type="checkbox"/> KZ Kazakhstan                                | <input type="checkbox"/> SK Slovakia                            |
| <input type="checkbox"/> CH & LI Switzerland and Liechtenstein | <input type="checkbox"/> LC Saint Lucia                               | <input type="checkbox"/> SL Sierra Leone                        |
| <input checked="" type="checkbox"/> CN China                   | <input type="checkbox"/> LR Sri Lanka                                 | <input type="checkbox"/> TJ Tajikistan                          |
| <input type="checkbox"/> CO Colombia                           | <input type="checkbox"/> LR Liberia                                   | <input type="checkbox"/> TM Turkmenistan                        |
| <input type="checkbox"/> CR Costa Rica                         | <input type="checkbox"/> LS Lesotho                                   | <input type="checkbox"/> TR Turkey                              |
| <input type="checkbox"/> CU Cuba                               | <input type="checkbox"/> LT Lithuania                                 | <input type="checkbox"/> TT Trinidad and Tobago                 |
| <input type="checkbox"/> CZ Czech Republic                     | <input type="checkbox"/> LU Luxembourg                                | <input type="checkbox"/> TZ United Republic of Tanzania         |
| <input type="checkbox"/> DE Germany                            | <input type="checkbox"/> LV Latvia                                    | <input type="checkbox"/> UA Ukraine                             |
| <input type="checkbox"/> DK Denmark                            | <input type="checkbox"/> MA Morocco                                   | <input type="checkbox"/> UG Uganda                              |
| <input type="checkbox"/> DM Dominica                           | <input type="checkbox"/> MD Republic of Moldova                       | <input checked="" type="checkbox"/> US United States of America |
| <input type="checkbox"/> DZ Algeria                            |   |   |
| <input type="checkbox"/> EE Estonia                            | <input type="checkbox"/> MG Madagascar                                | <input type="checkbox"/> UZ Uzbekistan                          |
| <input type="checkbox"/> ES Spain                              | <input type="checkbox"/> MK The former Yugoslav Republic of Macedonia | <input type="checkbox"/> VN Viet Nam                            |
| <input type="checkbox"/> FI Finland                            | <input type="checkbox"/> MN Mongolia                                  | <input type="checkbox"/> YU Yugoslavia                          |
| <input type="checkbox"/> GB United Kingdom                     |   | <input type="checkbox"/> ZA South Africa                        |
| <input type="checkbox"/> GD Grenada                            |   | <input type="checkbox"/> ZW Zimbabwe                            |

Check-boxes below reserved for designating States which have become party to the PCT after issuance of this sheet:

- |                          |                          |                          |
|--------------------------|--------------------------|--------------------------|
| <input type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> |
| <input type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> |

**Precautionary Designation Statement:** In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation (including fees) must reach the receiving Office within the 15-month time limit.)

**Box No. VI PRIORITY CLAIM**

The priority of the following earlier application(s) is hereby claimed:

Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application:* regional Office	international application: receiving Office
item (1) 09/06/2000	60/210,485	United States of America		
item (2)				
item (3)				
item (4)				
item (5)				

☐ Further priority claims are indicated in the Supplemental Box.

The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of this international application is the receiving Office) identified above as:

☐ all items    ☒ item (1)    ☐ item (2)    ☐ item (3)    ☐ item (4)    ☐ item (5)    ☐ other, see Supplemental Box

\* Where the earlier application is an ARIPO application, indicate at least one country party to the Paris Convention for the Protection of Industrial Property or one Member of the World Trade Organization for which that earlier application was filed (Rule 4.10(b)(ii)): .....

**Box No. VII INTERNATIONAL SEARCHING AUTHORITY**

Choice of International Searching Authority (ISA) (if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):

ISA/ US .....

Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):

Date (day/month/year)

Number

Country (or regional Office)

**Box No. VIII DECLARATIONS**

The following declarations are contained in Boxes Nos. VIII (i) to (v) (mark the applicable check-boxes below and indicate in the right column the number of each type of declaration):

Number of  
declarations

- |   |  |   |
|---|--|---|
| <input type="checkbox"/> Box No. VIII (i)   | Declaration as to the identity of the inventor   | : |
| <input type="checkbox"/> Box No. VIII (ii)  | Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent             | : |
| <input type="checkbox"/> Box No. VIII (iii) | Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application | : |
| <input type="checkbox"/> Box No. VIII (iv)  | Declaration of inventorship (only for the purposes of the designation of the United States of America)                               | : |
| <input type="checkbox"/> Box No. VIII (v)   | Declaration as to non-prejudicial disclosures or exceptions to lack of novelty   | : |

**Box No. IX CHECK LIST; LANGUAGE OF FILING****This international application contains:****(a) the following number of sheets in paper form:**

request (including declaration sheets) : 6  
 description (excluding sequence listing part) : 17  
 claims : 3  
 abstract : 1  
 drawings : 2  
**Sub-total number of sheets** : 29

sequence listing part of description (*actual number of sheets if filed in paper form, whether or not also filed in computer readable form; see (b) below*) : 0

**Total number of sheets** : 29

**(b) sequence listing part of description filed in computer readable form**

(i) ☐ only (under Section 801 (a)(i))

(ii) ☐ in addition to being filed in paper form (under Section 801 (a)(ii))

**Type and number of carriers** (diskette, CD-ROM, CD-R or other) on which the sequence listing part is contained (*additional copies to be indicated under item 9(ii), in right column*):

**This international application is accompanied by the following item(s) (mark the applicable check-boxes below and indicate in right column the number of each item):**

Number of items

1. ☒ fee calculation sheet
2. ☐ original separate power of attorney
3. ☐ original general power of attorney
4. ☐ copy of general power of attorney; reference number, if any: .....
5. ☐ statement explaining lack of signature
6. ☐ priority document(s) identified in Box No. VI as item(s): .....
7. ☐ translation of international application into (language): .....
8. ☐ separate indications concerning deposited microorganism or other biological material
9. ☐ sequence listing in computer readable form (indicate also type and number of carriers (diskette, CD-ROM, CD-R or other))
  - (i) ☐ copy submitted for the purposes of international search under Rule 13ter only (and not as part of the international application)
  - (ii) ☐ (only where check-box (b)(i) or (b)(ii) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under
  - (iii) ☐ together with relevant statements as to the identity of the copy or copies with the sequence listing part mentioned in left column
10. ☐ other (specify): .....

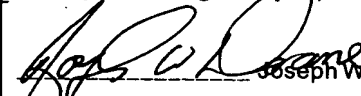
**Figure of the drawings** which should accompany the abstract: 1

**Language of filing of the international application:**

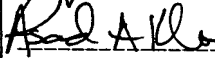
English

**Box No. X SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE**

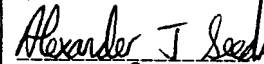
*Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).*



Joseph W. Doane (Inventor)



Asad A. Khan (Inventor)



Alexander J. Seed (Inventor)



Joel Domino - V. P. &amp; CFO, Kent Displays, Inc. (Applicant's Representative)

1. Date of actual receipt of the purported international application: 08 JUN 2001 (08.06.01)		2. Drawings:  <input type="checkbox"/> received:  <input type="checkbox"/> not received:
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:		
4. Date of timely receipt of the required corrections under PCT Article 11(2):		
5. International Searching Authority (if two or more are competent): ISA/US	6. <input type="checkbox"/> Transmittal of search copy delayed until search fee is paid	

Date of receipt of the record copy by the International Bureau:

For International Bureau use only

# PCT

## FEE CALCULATION SHEET

### Annex to the Request

For receiving Office use only

**PCT/US 01/14842**

International Application No.

**08 JUN 2001**

Date stamp of the receiving Office

Applicant's or agent's file reference <p style="text-align: center;"><b>KD-01-004PCT</b></p>	Applicant <p style="text-align: center;"><b>CHIRAL ADDITIVES FOR CHOLESTERIC DISPLAYS</b></p>
<b>CALCULATION OF PRESCRIBED FEES</b>	
1. TRANSMITTAL FEE	240.00 <span style="border: 1px solid black; padding: 0 5px;">T</span>
2. SEARCH FEE	700.00 <span style="border: 1px solid black; padding: 0 5px;">S</span>
International search to be carried out by <u>US</u> <i>(If two or more International Searching Authorities are competent to carry out the international search, indicate the name of the Authority which is chosen to carry out the international search.)</i>	
3. INTERNATIONAL FEE	
<b>Basic Fee</b> Where item (b) of Box No. IX applies, enter Sub-total number of sheets } <u>28</u> Where item (b) of Box No. IX does not apply, enter Total number of sheets } <u>28</u>	
<span style="border: 1px solid black; padding: 0 5px;">b1</span> first 30 sheets	427.00 <span style="border: 1px solid black; padding: 0 5px;">b1</span>
<span style="border: 1px solid black; padding: 0 5px;">b2</span> <u>0</u> x <u>10.00</u> =	0.00 <span style="border: 1px solid black; padding: 0 5px;">b2</span>
number of sheets fee per sheet	
<span style="border: 1px solid black; padding: 0 5px;">b3</span> additional component (only if sequence listing part of description is filed in computer readable form under Section 801(a)(i), or both in that form and on paper, under Section 801(a)(ii)):	
400 x _____ =	<span style="border: 1px solid black; padding: 0 5px;">b3</span>
fee per sheet	
Add amounts entered at b1, b2 and b3 and enter total at B . . .	
	427.00 <span style="border: 1px solid black; padding: 0 5px;">B</span>
<b>Designation Fees</b> The international application contains <u>5</u> designations. <u>5</u> x <u>92</u> =	
number of designation fees payable (maximum 6)	460.00 <span style="border: 1px solid black; padding: 0 5px;">D</span>
amount of designation fee	
Add amounts entered at B and D and enter total at I . . .	
	887.00 <span style="border: 1px solid black; padding: 0 5px;">I</span>
<i>(Applicants from certain States are entitled to a reduction of 75% of the international fee. Where the applicant is (or all applicants are) so entitled, the</i>	
4. FEE FOR PRIORITY DOCUMENT (if applicable)	15.00 <span style="border: 1px solid black; padding: 0 5px;">P</span>
5. TOTAL FEES PAYABLE	1,842.00
Add amounts entered at T, S, I and P, and enter total in the TOTAL box	
TOTAL	
<input type="checkbox"/> The designation fees are not paid at this time.	
<b>MODE OF PAYMENT</b>	
<input type="checkbox"/> authorization to charge <input type="checkbox"/> postal money order <input type="checkbox"/> cash <input type="checkbox"/> coupons <input checked="" type="checkbox"/> cheque <input type="checkbox"/> bank draft <input type="checkbox"/> revenue stamps <input type="checkbox"/> other (specify):	
<b>AUTHORIZATION TO CHARGE (OR CREDIT) DEPOSIT ACCOUNT</b> <i>(This mode of payment may not be available at all receiving Offices)</i>	
<input type="checkbox"/> Authorization to charge the total fees indicated above.	Receiving Office: RO/ <u>US</u>
<input checked="" type="checkbox"/> <i>(This check-box may be marked only if the conditions for deposit accounts of the receiving Office so permit)</i> Authorization to charge any deficiency or credit any overpayment in the total fees indicated above.	Deposit Account No.: <u>16-2372</u>
<input type="checkbox"/> Authorization to charge the fee for priority document.	Date: <u>08/06/2001</u>
	Name: <u>Raymond H. J. Powell, Jr.</u>
	Signature: <u><i>Raymond H. J. Powell, Jr.</i></u>

# PATENT COOPERATION TREATY

## PCT


### INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference <b>KD-01-004PCT</b>	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. <b>PCT/US01/14842</b>	International filing date (day/month/year) <b>08 June 2001 (08.06.2001)</b>	Priority date (day/month/year) <b>09 June 2000 (09.06.2000)</b>
International Patent Classification (IPC) or national classification and IPC <b>IPC(7): C09K 19/34, 19/32, 19/36; C07D 317/12 and US Cl.: lease See Supplemental Sheet.</b>		
Applicant <b>KENT DISPLAYS, INC.</b>		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 4 sheets, including this cover sheet.  
☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).  
These annexes consist of a total of 0 sheets.

3. This report contains indications relating to the following items:
  - I ☒ Basis of the report
  - II ☐ Priority
  - III ☐ Non-establishment of report with regard to novelty, inventive step and industrial applicability
  - IV ☐ Lack of unity of invention
  - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
  - VI ☐ Certain documents cited
  - VII ☐ Certain defects in the international application
  - VIII ☒ Certain observations on the international application

Date of submission of the demand <b>08 January 2002 (08.01.2002)</b>	Date of completion of this report <b>27 August 2002 (27.08.2002)</b>
Name and mailing address of the IPEA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703)305-3230	Authorized officer <b>Shean C. Wu</b>  Telephone No. 703-308-0661

Form PCT/IPEA/409 (cover sheet)(July 1998)

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US01/14842

## I. Basis of the report

## 1. With regard to the elements of the international application:\*

- ☒ the international application as originally filed.
- ☒ the description:  
pages 1-17 \_\_\_\_\_ as originally filed  
pages NONE \_\_\_\_\_, filed with the demand  
pages NONE \_\_\_\_\_, filed with the letter of \_\_\_\_\_.
- ☒ the claims:  
pages 18-20 \_\_\_\_\_, as originally filed  
pages NONE \_\_\_\_\_, as amended (together with any statement) under Article 19  
pages NONE \_\_\_\_\_, filed with the demand  
pages NONE \_\_\_\_\_, filed with the letter of \_\_\_\_\_.
- ☒ the drawings:  
pages 1-2 \_\_\_\_\_, as originally filed  
pages NONE \_\_\_\_\_, filed with the demand  
pages NONE \_\_\_\_\_, filed with the letter of \_\_\_\_\_.
- ☐ the sequence listing part of the description:  
pages NONE \_\_\_\_\_, as originally filed  
pages NONE \_\_\_\_\_, filed with the demand  
pages NONE \_\_\_\_\_, filed with the letter of \_\_\_\_\_.

## 2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language \_\_\_\_\_ which is:

- ☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

## 3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in printed form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. ☒ The amendments have resulted in the cancellation of:

- ☒ the description, pages none
- ☒ the claims, Nos. none
- ☒ the drawings, sheets/fig none

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).\*\*

\* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

\*\* Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.  
PCT/US01/14842

## V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

### 1. STATEMENT

Novelty (N)

Claims 1-17 YES  
Claims none NO

Inventive Step (IS)

Claims 1-17 YES  
Claims none NO

Industrial Applicability (IA)

Claims 1-17 YES  
Claims none NO

### 2. CITATIONS AND EXPLANATIONS

Claims 1-17 meet the criteria set out in PCT Article 33(2)-(4), because the prior art does not teach or fairly suggest by prior art. The present invention has an additional group R<sub>4</sub> attached to naphthalene ring, which R<sub>4</sub> is a hydrocarbon. The prior art only discloses dioxolane derivatives without substituted naphthalene ring.

----- NEW CITATIONS -----  
NONE

----- NEW CITATIONS -----

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US01/14842

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the questions whether the claims are fully supported by the description, are made:

Claims 2-3 and 5-12 are objected to as lacking clarity under PCT Rule 66.2(a)(v) because practice of the claimed invention is not adequately described in writing, as required under PCT Rule 5.1(a)(iii), for the reasons set forth in the immediately preceding paragraph.

The coefficient  $n$  in notation  $R_n$  does not have an upper limit. The language "0 or 1 or more" is not clearly defined for  $n$  value.